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Thermally Controlled Water Injection into BH_4-Sodalite for Hydrogen Formation Investigated by IR Absorption

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Infrared absorption spectroscopy was used to investigate the mechanism of hydrogen release from borontetrahydride sodalite, $Na_8[AlSiO_4]_6(BH_4)_2$. The hydrogen formation follows the reaction

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2 \quad (1)$$

via consecutive intra-cage reaction steps. Water molecules are injected through X-ray amorphous hydrosodalite species which are formed simultaneously with the borontetrahydride sodalite during synthesis. The synthesis procedure of borontetrahydride-sodalite, $Na_8[AlSiO_4]_6(BH_4)_2$, followed that described by Buhl *et al.* [1]. Infrared spectra were taken using a FTIR spectrometer (Bruker IFS66v) with KBr and NaCl pressed pellets, a home-made Ag sample holder and heating device as described in Ref. [2].

Borontetrahydride sodalite, $Na_8[AlSiO_4]_6(BH_4)_2$, shows the sodalite typical peaks of the framework vibrations at 450, 500, 666, 707, 734 and 1000 (all in cm^{-1}). The peaks at 1143 (ν_4), 2286 ($2*\nu_4$), 2241 (ν_3) and 2390 ($\nu_{2+}\nu_4$) can be assigned to vibrations of the BH_4^- tetrahedral group by direct comparison to the spectrum of pure sodium borontetrahydride salt (Fig. 1). For the BH_4^- related absorption a strong broadening and decrease in peak height is observed with increasing temperature already at 150 °C which could be related to the dynamical rotation due to a high degree of freedom. Indications of a new peak (A in Fig. 1) appear which increases in intensity and becomes clearly visible at 350 °C and when the sample is cooled down again. The A feature indicates the first reaction step which leads to a release of hydrogen related with a small (less than about 5%) decrease in the intensity of the BH_4^- related peaks. The sodalite sample shows a weak absorption feature at about 1650 cm^{-1} and a broad feature in the range between 3200 to 3700 cm^{-1} (D in Fig. 1) indicating the presence of H_2O species. A sharper OH absorption feature is observed at about 3620 cm^{-1} (D′ in Fig. 1). The broad H_2O related feature gradually decreases in intensity with increasing temperature up to 350 °C and the sharper OH peak D′ remains, which can be similarly observed in basic sodalites [3]. Cooling down again to 20°C shows that even the broader peak D still appears to some extent, indicating a remaining water content. The loss in intensity of peak D is related to the water content consumed for the release of hydrogen for temperatures up to 350 °C and for the further heating. The origin of features D and D′ can thus be related to some X-ray amorphous (basic) hydro-sodalite type of material which is formed simultaneously with the borontetrahydride sodalite during synthesis. In the present case the X-ray amorphous

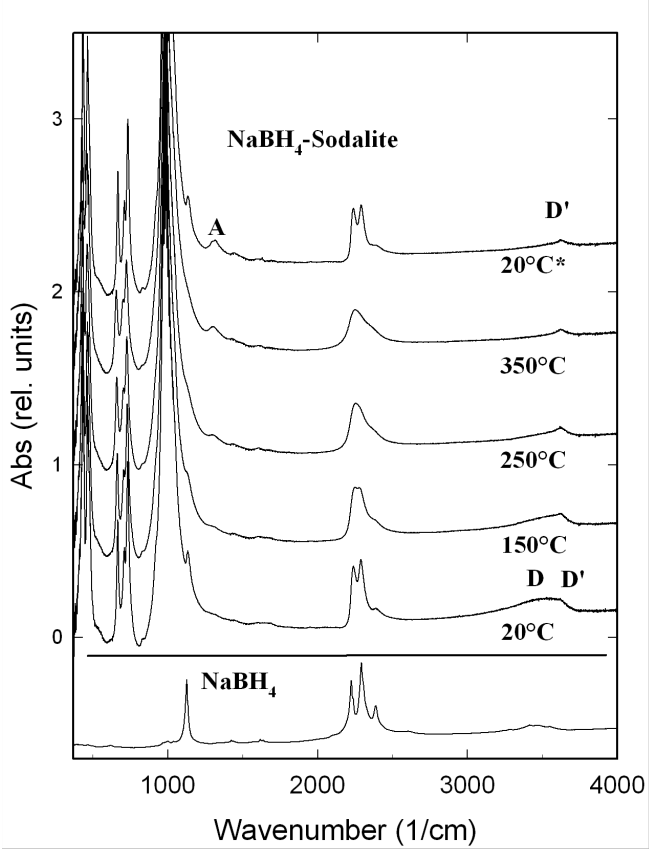

Fig. 1 Spectra of $NaBH_4$ and $NaBH_4$ enclathrated in soldalite at temperatures (*in situ*) as given. 20 °C* denotes the spectrum obtained after cooling down from 350 °C.

part can be estimated to about 5 to 10 percent by weight. In a combination of experiments with heating up to 500 °C and characterisation by infrared absorption spectra it was also observed that the residual water content further reacts up to about 20 % of the total BH_4^- content as described by the reaction (1) and then stops. The sodalite containing the formed borate species remains stable at 500 °C. However, reaction (1) can be further continued after reloading the hydrosodalite type part of the sample with water. This was done at 20 °C under room ambient conditions being characteristic of hydrosodalite. It was observed that in this way the total BH_4^- content was consumed in about 10 further runs of cooling down from 500 °C, reloading with water and reheating and so forth.

Details of the formation of BO_2^- intra-cage species and the nearly complete disappearance of BH_4^- absorption intensities is shown in another IR experiment with a heating up to 600 °C in Fig. 2. The BO_2^- absorption signature is denoted by C for the spectrum obtained after cooling to room temperature. The absorption feature denoted by B indicates another intermediate step which occurs within the reaction towards the final products as given in (1). The intensity of A becomes reduced when B increases and B becomes reduced again when C increases showing the nature of consecutive reactions involved in (1). The part of the hydro-sodalite type species with its water content can only account for a total reaction of not more than 20 % of the borontetrahydride sodalite, and further reaction requires reloading of the hydrosodalite with water. Therefore the observation that the BH_4^- peak disappeared in the experimental results shown in Fig. 2 implies that the water molecules are gained from the (wet) NaCl matrix. The loss of water content from the NaCl plus sample pellet during heating can be seen by the appearance of a "negative absorption" peak marked as HOH_{NaCl} in Fig. 2. The peak marked by HOH_{Sod} can be assigned to the water content of the hydro-sodalite type contribution as a (wet) NaCl-

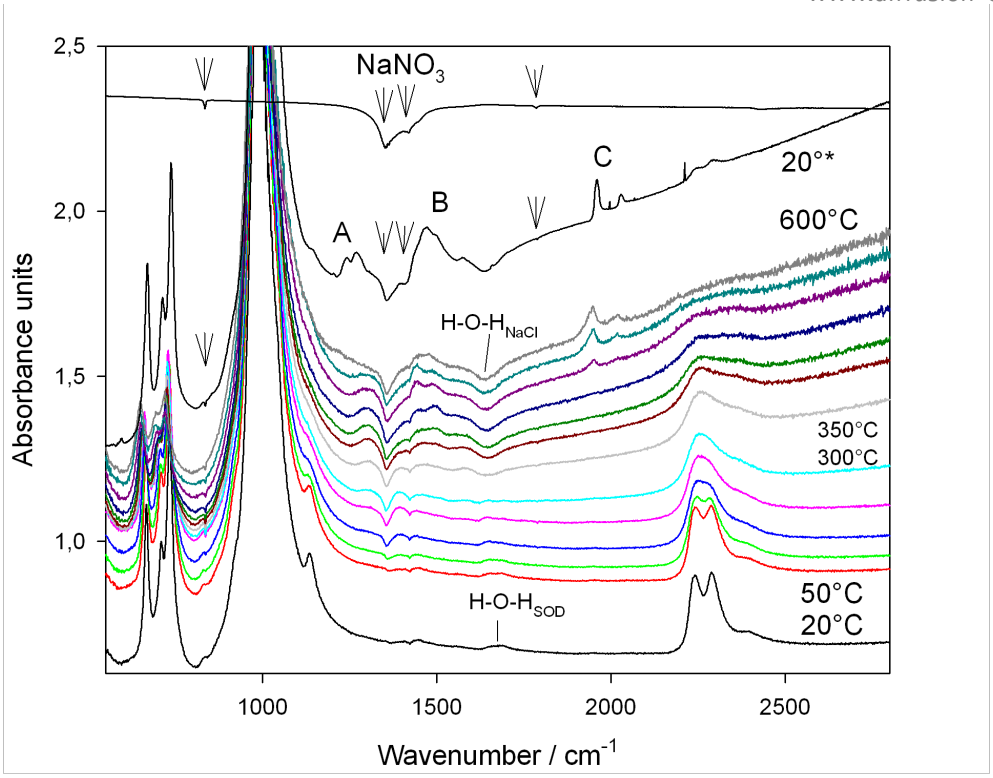

Fig. 2 IR *in situ* experiment in NaCl, in steps of 50 °C. 20 °C* denotes the spectrum after cooling. Arrows mark the effect of tracer reaction of $NaNO_3$ and H_2.

pellet was used as reference, *i.e.*, the effect of the water content corresponding to NaCl matrix is cancelled out in the spectrum taken at 20 °C, but becomes negative for water loss larger than the content of HOH_{Sod}. A further "negative absorption" signature is marked by arrows in Fig. 2. This effect can be explained by a reduction reaction of sodium nitrate induced by the hydrogen release which was supplied to the NaCl matrix by a special evaporation technique. A spectrum of sodium nitrate is given in Fig. 2 with a negative scaling for better comparison which proves the correct interpretation.

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